Utilization of Coal-Tar Pitch in Insulating-Seal Materials

Janusz Zieliński
Technical University of Warsaw
Branch at Płock
Institute of Chemistry
Płock, Poland

George Górecki
Ardrox, Incorporated
921 Sherwood Drive
Lake Bluff, IL 60044

Substances obtained from coal, in light of their physicochemical properties, can find a number of interesting applications. Among these substances are tars and coal-tar pitch. Collin (1) has described a variety of applications using coal-tar pitch (see Fig. 1). The majority of these applications, however, are realized only in a narrow scope. At the industrial level, pitch is most often treated as a by-product of the process of continual distillation of coal-based tar. One path that leads to the improvement of thermal and rheological properties of bitumens derived from coal is their modification by means of the addition of polymers. This creates the possibility of attaining greater utility from coal-tar pitch. One example is the improvement of binder quality in insulating-seal materials. This capability permits, in a relatively straightforward manner, the application of coal-tar pitch on a large scale. We feel that, in addition to the applications of pitch described by Collin, it is important to understand that pitch can be used as a binder or as a base substance in insulating-seal materials for the building, road construction and machinery industries.

Compositions based on petroleum asphalts are examples confirming the usefulness of this approach. The literature pertaining to the modification of petroleum bitumens by polymers is very extensive, the majority of which has been published in patents. For the most part, these works deal with the physical modification of asphalts by means of plastics, with the intention of obtaining homogeneous mixtures (2-6). Polymers produce diverse changes in the properties of petroleum bitumen. This is related mostly to an increase in stability and durability of the bitumen's physico-colloidal structure (7).

On the other hand, combining coal-tar pitch with polymers has generated a significantly smaller level of interest. Nevertheless, various types of polymers have been utilized to modify the properties of tars and coal-tar pitch. These polymers provided the means of attaining homogeneous and stable compositions. In particular, the goal of these works was to obtain binders used in the building of roads (8) and in tar-based lacquers (9). At present, the mechanisms for the composition of coal-tar pitch/polymer mixtures has not been elucidated. Neither has the interaction between these two types of constituents been distinctly explained. In both petroleum-asphalt/polymer compositions and pitch-polymer arrangements, it is accepted that homogeneity is the uniform dispersion of (a) polymer particles and (b) elements of resinous asphaltene pitch in its oil phase. Mutual interactions between the continuous phase of the bitumen (low molecular weight oils and resins) and the polymer as well as between the polymer and the dispersed phase of the pitch (resinous and asphaltenic substances, beta- and gamma- forms) determine the final physico-colloidal structure of the composition (7). Compared to petroleum asphalts, coal-tar pitch comprises relatively small amounts of the continuous phase. It is therefore appropriate to enrich coal-tar pitch with additional plasticizing substances.

The goal of the investigations was to determine the pitch-polymer composition which would fill the role of the matrix, having as a basis high-molecular weight insulating-seal materials. The investigations were carried out in two stages.

In the first stage, problems relating to the attainment of homogeneous and stable compositions made from the chosen types of polymers, plasticizers and coal-tar pitch were investigated. The first stage is outlined in Fig. 2. In the second stage, the formulations of the compositions were established. These mixtures were able to define beneficial characteristics for bituminous insulating-seal materials.

The following materials were studied:

1. Normal coal-tar pitch at its softening point of 87°C as well as the contents of components insoluble in toluene (21.45%).

2. Polymers. Atactic polypropylene (aPP, molecular weight: 32,600); isotactic polypropylene (iPP, MW: 220,000) with an isotactic index above 95%; polyvinyl chloride (PVC, MW: 139,000); polystyrene (PS, MW: 304,000); styrene-butadiene rubber latex containing 24.5% combined styrene and 59% rubber substances.

3. Plasticizers. Dibutyl phthalate; anthracene oil; furfurol extract.

4. Fillers. Milled chalk; talc; colloidal silica.

The following determinations were performed on the obtained compositions:

1. Fragility point (Fraass).

2. Softening point (Pierscien and Kula).

3. Penetration and stability at elevated temperatures according to the Tube Test (10). The stability index was determined from the mutually relative densities of upper and lower layers of samples heated to 150°C for 4 days.

4. Adhesion. Concrete, glass, wood and aluminum were used as substrates.

5. Flow along vertical surfaces.

6. Resistance to freezing.

7. Elasticity at negative temperatures, as low as -20°C.

8. Aging tests. Twenty cycles, where one cycle lasted 48 hr and involved exposure to UV radiation, artificial rain and heating to 70°C and freezing to -25°C.

In the case of compositions made up of coal-tar pitch and polymers, certain intrinsic factors play a particular role with regard to obtaining mixtures which are homogeneous and which will not delaminate. These factors include: temperature, the time needed to reach homogeneity and the order of addition of components. Another important factor is the elimination of circumstances which may destroy the polymers.

The polymers that were examined differed in structure and characteristics. Beneficial properties were attained only in the case where pitch was combined with polar PVC. Mixtures containing 10% w/w PVC in pitch were homogeneous and stable. The addition of PVC increased the softening point to 114°C, with a concurrent lack of improvement in elasticity.

In the cases involving other polymers, the results were not as fruitful. Differences in the chemical make-up and the colloidal structure of pitch and PP prevented the attainment of mixtures that did not delaminate. In order to obtain homogeneous mixtures of pitch and PS, a temperature range of 260-310°C was required. This led to the destruction of the polymer and provided no changes in the properties of the pitch.

Plastification of pitch by means of oil fractions that are coal-based (anthracene oil) and petroleum-based (fuel oil, furfurol extract), as well as artificially-produced dibutyl phthalate obtained from industry was studied. It was demonstrated that the most beneficial changes in properties were obtained using dibutyl phthalate at 25-30% w/w. The dibutyl-phthalate-modified pitch provided new qualities in pitch-plasticizer binders. For example, the fragility point (according to Fraass) of pitch-phthalate mixtures is -24°C. Mixtures of pitch and furfurol extract or anthracene oil at 20-25% w/w provided similar improvements.

In order to be eventually applied as base substances for insulating-seal materials, two-component mixtures of pitch-polymer and pitch-plasticizer required further modification. This was made possible by improving their mechanico-rheological properties. The three-component systems were comprised of coal-tar pitch, polymers and plasticizers. The best properties were obtained by compositions having 25% w/w dibutyl phthalate relative to pitch and 5-8% w/w PVC relative to pitch-plasticizer binder. Phthalate was used as plasticizer because it efficiently enabled the elimination of the elastomeric properties of PVC in a pitch environment.

The compositions were also modified with styrene-butadiene rubber in order to impart resistance to elevated temperatures and to provide high elasticity at negative temperatures. The following composition provides advantageous properties: coal-tar pitch (58.6% w/w), phthalate (22%), PVC (7.4%), styrene-butadiene rubber latex (7.4%). The fragility point of this mixture was -36°C and the softening point was 58°C. The penetration at 25°C was about 100 x 10^{-4} m and the stability index was 0.4%. These properties permitted the mixture to behave like an insulating-seal material.

The second part of the investigation involved determining the formulation of the final mixture, which had coal-tar pitch as a fundamental component. The composition was defined by standard specifications used for dilatant putties and hydroinsulation linings used in the building industry. As a rule, fillers and adhesion agents comprise materials of this type. The influence of the types and amounts of fillers (milled chalk, talc, colloidal silica) as well as that of adhesive media (balmy rosin, coumarone-indene resin) on the properties of butadiene-styrene pitch-phthalate-PVC-latex mixtures was studied. It was found that, regardless of the choice of filler, the most beneficial changes in applied properties were attained with filler mixtures containing chalk or talc with colloidal silica in a mass ratio of 4:1. Testing was performed by examining levelling at higher temperature, vertical flow at 60°C, resistance to freezing at -10°C and -20°C. At the same time, the amount of filler in the entire substance, depending on the application, should be 15-30% w/w. On the other hand, balmy rosin, in quantities of 2-3% w/w, was used as the adhesive agent. The rosin increases cohesion between the binder and the fillers. This provides an increase in the breaking strength (>0.1 MPa).

The results of the investigation provided the optimal formulations, which are listed in Table I. These compositions have many practical applications, such as the filling of horizontal slits in concrete as well as strengthening the bonds between metal-glass and wood-glass interfaces. Other applications include bituminous dilatant putties, sealing vertical surfaces in building elements, and hydroinsulating linings (1-3 mm thickness) formed by the hot rolling method, for use in the building industry.

The thermomechanical, rheological and practical properties of these compositions are comparable to the properties of analogous mixtures based on petroleum asphalts. In some instances, the properties of the pitch-based mixtures exceed those of the petroleum-based ones (e.g., adhesion to concrete, metallic or glass substrates). Modified pitch-polymer compositions can be used in general and specialized building applications. Examples include the construction of roads, airports, underground objects. Other examples can be found in the machine industry, where these mixtures are used as materials to prevent water penetration and to deaden vibrations.

References

1. G. Collin, Production and Application of Coal-Tar Pitch, International Conference on Structure and Properties of Coals, 154, 1991.

2. US Patent 4,430,464, 1984.

3. UK Patent 1,457,999, 1976.

4. J. Zieliński, Erdol u. Kohle, Erdgas, Petrochemie, **42**, 456, 1989.

5. G. Collin and M. Zander, Erdöl u. Kohle, Erdgas, Petrochemie, **39**, 517, 1986.

6. J. Zieliński and A. Bukowski, Ropa a Uhlie, **29**, 404, 1987.

7. J. Zieliński, The Studying of Structure and the Properties of Bitumen-Polymer Compositions, Wyd. Politechniki Warszawskiej, Seria Chemia, 1991.

8. Z. Stompel, et. al., Koks, Smoła, Gaz, **33**, 24, 1989.

9. J. Kozakiewicz, et. al., Polimery, **37**, 534, 1992.

10. G. Zenke, Bitumen, 1, 11, 1973.

TABLE I - OPTIMAL QUANTITIES of COMPONENTS

Component	Sealing Compound (% w/w)	Sealing putty (% w/w)	Pitch-polymer lining (% w/w)
Coal-tar pitch	56.10	48.90	48.30
Dibutyl phthalate	18.70	16.30	16.10
PVC	6.50	5.70	7.10
Styrene-butadiene rubber latex	6.50	5.70	7.10
Talc	9.76	--	17.10
Milling chalk	--	17.00	--
Colloidal silica	2.44	4.30	4.30
Balmy rosin	--	2.10	--

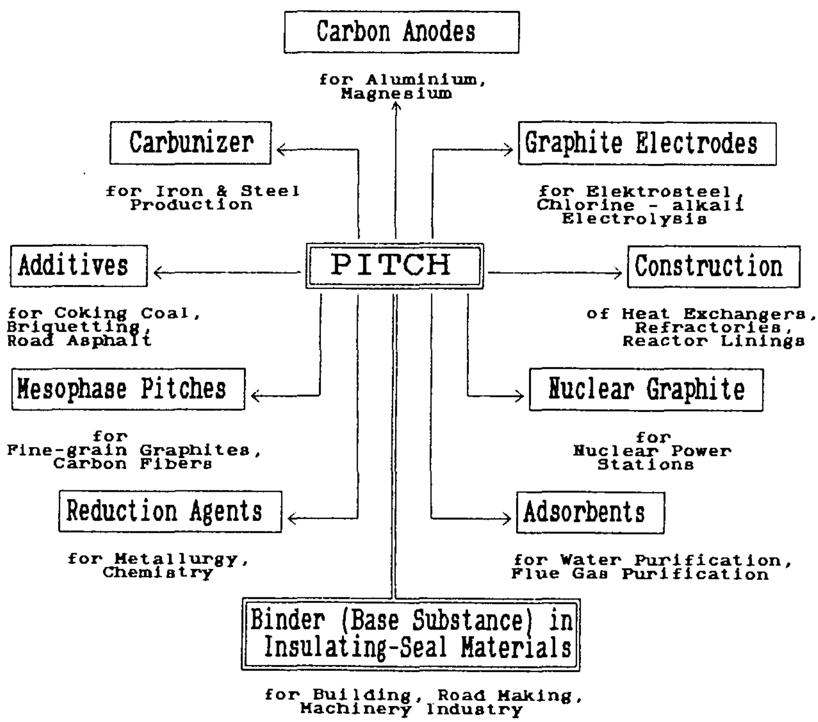

Fig.1. Application of Coal-Tar Pitch [G.Collin]

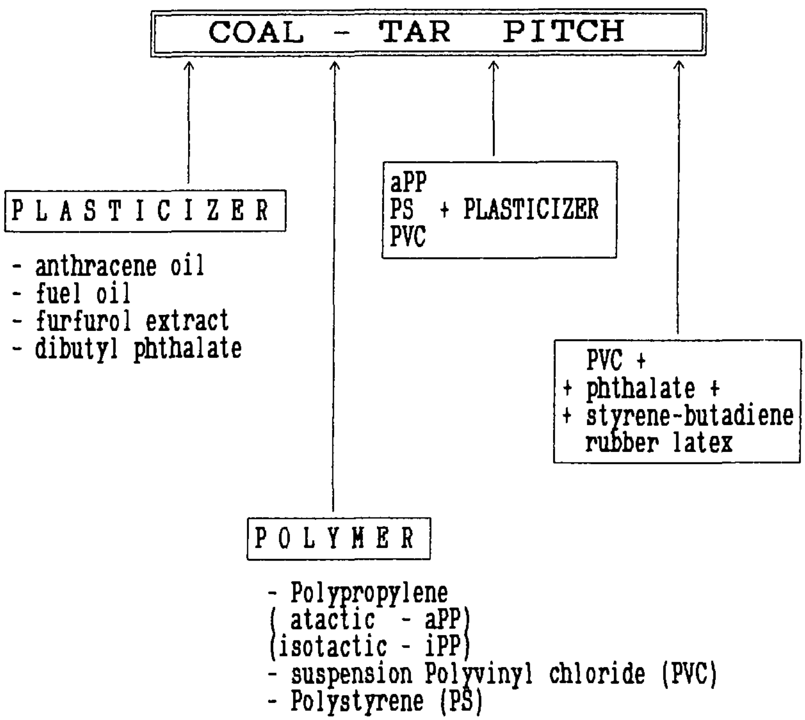

Fig. 2. Essential directions of investigation concerning modification of properties of coal-tar pitch